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LEAD–ANTIMONY SULFOSALTS FROM TUSCANY (ITALY). VIII. ROUXELITE, Cu$_2$HgPb$_{22}$Sb$_{28}$S$_{64}$(O,S)$_2$, A NEW SULFOSALT FROM BUCA DELLA VENA MINE, APUAN ALPS: DEFINITION AND CRYSTAL STRUCTURE

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ABSTRACT

Rouxelite, Cu$_2$HgPb$_{22}$Sb$_{28}$S$_{64}$(O,S)$_2$, is a new species of sulfosalt discovered in the Buca della Vena Fe–Ba deposit, Apuan Alps, Italy. It occurs as acicular metallic crystals in calcite veins; reflectance values in air are (R%, λ in nm): 38.2 (470), 36.2 (546), 35.4 (589), 32.8 (650). Rouxelite is monoclinic, space group *C*2/*m*, with *a* 43.113, *b* 4.059, *c* 37.874 Å, β 117.35°, *V* 5887 Å^3, *Z* = 2, D$_{calc}$ = 5.86 g/cm^3. The eight most intense lines of the X-ray powder-diffraction pattern [*d* (in Å)(*I*)(*hkl*)] are: 3.84(31)($\overline{10}$.0.8), 3.402(100)($\overline{10}$.0.2, $\overline{12}$.0.8, 115), 3.369(74)($\overline{7}$14, 0.0.10), 2.815(70)(317, $\overline{11}$.1.4), 2.756(36)(516, 12.0.3), 2.251(31)(1.1.12, 3.1.11), 2.116(31)($\overline{11}$.1.15), and 1.955(30)($\overline{19}$.1.5, 11.1.8). Electron-microprobe analyses gave (wt.%; mean of six spot analyses): Cu 1.34(5), Hg 1.76(9), Pb 45.08(15), Sb 31.50(14), S 20.07(11), O (struct.) 0.20, sum 99.95. The chemical formula, calculated on the basis of a cation total of 53 atoms, is Cu$_{2.20}$Hg$_{0.92}$Pb$_{22.78}$Sb$_{27.10}$S$_{65.53}$O$_{1.31}$ (*Z* = 2), giving the idealized formula Cu$_2$HgPb$_{22}$Sb$_{28}$S$_{64}$(O,S)$_2$, which is charge-balanced. An X-ray single-crystal study, despite a poor *R* value (0.169), revealed a quite original structure, with Cu and Hg in two specific sites, a tetrahedral one for Cu, and a flattened octahedral one for Hg. There is also a split O,S position, bound to two Sb atoms. For the main part, Pb, Sb and S atoms are organized in columns with a pseudoternary axis, derived from hexagonal Ba$_{12}$Bi$_{24}$S$_{48}$. The structural formula is Cu$_2$HgPb$_{22.6}$Sb$_{27.4}$S$_{64.67}$O$_{1.33}$. The structure is built up of two types of ribbons parallel to *b* and alternating along *a*, rimmed by a ribbon-layer parallel to (010); the result is a three-component structure of the boxwork type, like for neyite. Very large topologically equivalent columns are also recognizable in rouxelite and kobellite, which have about 90% of their structure motif in common. The formation of rouxelite is associated with the hydrothermal remobilization and deposition of mercury in the Apuan Alps during the Apenninic tectonometamorphic event, as illustrated in the nearby Hg deposits of Ripa and Levigliani. The name honors Jean Rouxel (1935–1998), solid state chemist, professor and founder of the Institut des Matériaux, University of Nantes (France).

Keywords: rouxelite, new mineral species, sulfosalt, lead, antimony, mercury, crystal structure, Tuscany, Italy.

SOMMAIRE

La rouxélite, Cu$_2$HgPb$_{22}$Sb$_{28}$S$_{64}$(O,S)$_2$, est une nouvelle espèce de sulfosel découverte dans le gisement à Fe–Ba de Buca della Vena (Alpes Apuanes, Italie). Elle se présente en cristaux aciculaires à éclat métallique dans des veines de calcite. Réflectance dans l'air (R%, λ en nm): 38.2 (470), 36.2 (546), 35.4 (589), 32.8 (650). La rouxélite est monoclinique, groupe d'espace *C*2/*m*, avec *a* 43.113, *b* 4.059, *c* 37.874 Å, β 117.35°, *V* 5887 Å^3, *Z* = 2, D$_{calc}$ = 5.86 g/cm^3. Les huit principales raies du diagramme de poudre en diffraction X [*d* en Å(*I*)(*hkl*)] sont: 3.84(31)($\overline{10}$.0.8), 3.402(100)($\overline{10}$.0.2, $\overline{12}$.0.8, 115), 3.369(74)($\overline{7}$14, 0.0.10), 2.815(70)(317, $\overline{11}$.1.4), 2.756(36)(516, 12.0.3), 2.251(31)(1.1.12, 3.1.11), 2.116(31)($\overline{11}$.1.15), 1.955(30)($\overline{19}$.1.5, 11.1.8). L'analyse à la microsonde électronique donne (% poids, résultat moyen de six analyses): Cu 1.34(5), Hg 1.76(9), Pb 45.08(15), Sb 31.50(14), S 20.07(11), Total 99.95. La formule chimique, sur la base d'un total de 53 cations, est Cu$_{2.20}$Hg$_{0.92}$Pb$_{22.78}$Sb$_{27.10}$S$_{65.53}$O$_{1.31}$, conduisant à la formule stœchiométrique équilibrée Cu$_2$HgPb$_{22}$Sb$_{28}$S$_{64}$(O,S)$_2$. L'étude aux rayons X sur monocristal, malgré une valeur médiocre de R (0.169), révèle une structure tout à fait originale, avec Cu et Hg dans deux sites spécifiques, tétraédrique pour Cu et octaédrique aplati pour Hg. Il y a également une position éclatée pour O,S, liée à deux atomes de Sb. Une majorité des atomes de Pb, Sb et S forment des colonnes organisées autour de pseudo-axes ternaires, dérivées de Ba$_{12}$Bi$_{24}$S$_{48}$ hexagonal. La formule structurale est Cu$_2$HgPb$_{22.6}$Sb$_{27.4}$S$_{64.67}$O$_{1.33}$. La structure résulte de la combinaison de deux types de rubans parallèles à *b*, en alternance suivant *a*, bordés par un feuillet-palissade parallèle à (010). Cette

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architecture combinant trois modules donne une structure du type "boxwork", comme pour la neyite. Des domaines très étendus équivalents sur le plan topologique sont également reconnaissables entre la rouxélite et la kobellite, qui ont environ 90% de leur motif structural en commun. La formation de la rouxélite paraît subordonnée à la remobilisation et au dépôt hydrothermaux du mercure dans les Alpes Apuanes lors de la phase tectono-métamorphique apennine, à l'instar des gisements de mercure voisins de Ripa et Lévigliani. Cette nouvelle espèce est dédiée au Professeur Jean Rouxel (1935–1998), chimiste du solide, fondateur de l'Institut des Matériaux à l'Université de Nantes (France).

Mots-clés: rouxélite, nouvelle espèce minérale, sulfosel, plomb, antimoine, mercure, structure cristalline, Toscane, Italie.

INTRODUCTION

Buca della Vena, a small Fe–Ba deposit in the Apuan Alps (Benvenuti *et al*. 1986), presents a complex mineralogy (Orlandi & Checchi 1986, Orlandi & Dini 2004). Many lead–antimony sulfosalts are present, and three new ones have recently been defined: scainiite, pillaite and pellouxite (Orlandi *et al*. 1999, 2001, 2004). The present study deals with a fourth new sulfosalt, rouxelite ("rouxélite" in French, according to phonetic rules). This new mineral and its name have been approved by the CNMMN of the IMA (No 2002–062). The name honors Jean Rouxel (1935–1998), specialist of solid-state chemistry and member of the French Academy of Sciences. Founder of the "Institut des Matériaux" at Nantes, Professor Rouxel was particularly active in the study of chemical bonding and physical properties of low-dimensional chalcogenides; he favored the study of natural sulfides as a source of references for new materials. The type material of rouxelite is deposited at Museo di Storia Naturale e del Territorio, Università di Pisa.

The small Ba and Fe-oxide deposit of Buca della Vena is located near the village of Ponte Stazzemese, in the Apuan Alps. The geological setting as well as the ore parageneses have been presented elsewhere (Orlandi & Checchi 1986, Orlandi *et al*. 1999). Like the other lead sulfosalts, rouxelite was formed in the latest stage of hydrothermal activity, within small veinlets cross-cutting dolomitic lenses interstratified in the Ba–Fe ore. It is closely associated with bournonite; tetrahedrite and sphalerite also were observed in the same veinlets.

The characterization of rouxelite led to the identification of a second occurrence of this new species in a polished section from the antimony deposit of Magurka, Slovakia (sample 47 of T. Řídkošil; Y. Moëlo, unpubl. data, 1990). The sample is constituted mainly of boulangerite, with some pyrite, Hg-bearing sphalerite (0.8 wt.% Hg, 0.1% Fe) and bournonite, in a gangue of quartz. There are very few crystals of rouxelite, disseminated within bournonite, or close to it.

MINERALOGICAL CHARACTERIZATION

Appearance and physical properties

Rouxelite is very rare, and only a few crystals could be identified among hundreds of fibers of lead sulfosalt examined by X-ray diffraction. It occurs as black acicular crystals with a metallic luster, elongated and striated parallel to [010] (Fig. 1). Its hardness could not be determined owing to the small size and scarcity of the crystals. No cleavage was observed, and the crystal structure (see below) does not present any infinite surface of weak bonding that would favor such a cleavage.

In reflected light, rouxelite is light grey, with a weak bireflectance, without pleochroism. Between crossed polars, the anisotropy is distinct, higher than that of boulangerite, and similar to that of robinsonite, without polarization tints. Reflectance data in air are given in Table 1. The reflectance curve (Fig. 2) decreases regularly, as is generally the case for lead–antimony sulfosalts (Criddle & Stanley 1993). Density could not be measured owing to the paucity of this sulfosalt. According to the empirical formula resulting from the crystal-structure determination, $D_{calc} = 5.89$ g/cm^3, compared with 5.86 g/cm^3 for $Cu_2HgPb_{22}Sb_{28}S_{64}(O,S)_2$, the stoichiometry of this new species.

Chemical composition

Qualitative SEM–EDS chemical analysis of rouxelite showed major amounts of lead, antimony and sulfur, with minor amounts of copper and mercury. Electron-probe micro-analysis (EPMA) was performed on a Cameca SX 50 apparatus (common laboratory BRGM–CNRS–Université d'Orléans, France). Oper-

TABLE 1. ROUXELITE: REFLECTANCE DATA IN AIR

λ	R_{air}	λ	R_{air}	λ	R_{air}	λ	R_{air}
400	39.3	500	37.7	600	34.8	700	30.8
410	38.8	510	37.7	610	34.4	710	30.0
420	38.5	520	37.0	620	33.7	720	30.3
430	38.1	530	37.0	630	33.9	730	29.2
440	39.2	540	36.4	640	33.4	740	29.0
450	39.0	550	36.2	650	32.8	750	28.8
460	39.0	560	36.1	660	32.5	760	28.8
470	38.2	570	35.4	670	31.9	770	28.9
480	38.3	580	35.2	680	31.4	780	28.2
490	37.8	590	35.3	690	31.0	790	26.5
						800	25.2
470	38.2	**546**	36.2	**589**	35.4	**650**	32.8

Wavelength λ in nm, R_{air} in %. Polishing method: 6, 1 , ¼ and $^1/_{10}$ diamond cloth; final buffing with Cr_2O_3 on cloth. LEICA DMR microscope with FLUOTAR 20×/0.50 POL objective. Microscope photometer: Leica MPV–SP, monochromator: Δλ = 2 nm. Standard: SiC (NPL 50). Random section.
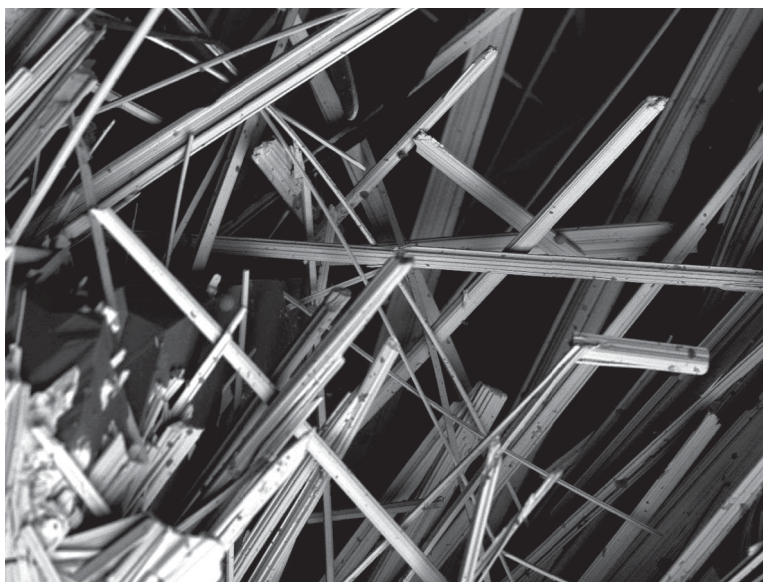
Fig. 1. SEM image of rouxelite fibers and laths. The largest crystals are about 2 mm in length.

ating conditions were as follows: 20 kV (10 kV for oxygen), 20 nA, standards [element (*emission line*, counting time for one spot analysis)]: PbS (Pb$M\alpha$, 20 s), pyrite (S$K\alpha$, 10 s), stibnite (Sb$L\alpha$, 10 s), Cu metal (Cu$K\alpha$, 10 s), HgS (Hg$M\alpha$, 20 s), SnO$_2$ (O$K\alpha$, 10 s). Analytical results are presented in Table 2. As in the case of pillaite (Orlandi *et al*. 2001), the oxygen content is very low (0.39 wt.%), and not significant by itself, as it reflects the probable presence of an oxidation film on the surface of the sample.

On the basis of a total of 53 cations, the formula resulting from the EPMA data is Cu$_{2.20}$Hg$_{0.92}$Pb$_{22.78}$Sb$_{27.10}$S$_{65.53}$O$_{2.55}$, very close (except for oxygen) to the formula inferred from the crystal-structure study, Cu$_2$HgPb$_{22.6}$Sb$_{27.4}$S$_{64.67}$O$_{1.33}$. The idealized stoichiometric formula, which is charge balanced, is Cu$_2$HgPb$_{22}$Sb$_{28}$S$_{64}$(O,S)$_2$.

An old set of EPMA data (Y. Moëlo, unpubl., 1990) acquired on a sample from Magurka (Slovakia), clearly corresponds to a second occurrence of rouxelite, as mentioned in the Introduction (Table 2). The amounts of all elements are very close to the current result, except for a lower Hg content (1.07 wt.%), compensated by a significant Ag content (0.35 wt.%). The formula (mean result of seven analyses, oxygen not considered) is: Cu$_{2.08}$Ag$_{0.33}$Hg$_{0.55}$Pb$_{22.80}$Sb$_{27.24}$S$_{64.38}$.

X-ray data

Rotation, Weissenberg and precession photographs indicated that rouxelite is monoclinic, space group

$C2/m$, with *a* 43.113, *b* 4.059, *c* 37.874 Å, β 117.35°, *V* 5887 Å^3, *Z* = 2. According to rotation films, there is a 2*b* superstructure, as indicated by very weak *h*1*l* reflections. The X-ray powder-diffraction pattern (Table 3) was obtained with a Gandolfi camera, and is compared with the simulated pattern calculated from the crystal structure (FULLPROF program) on the basis of the subcell. The most intense lines [*d* (in Å)(*I*)(*hkl*)] are: 3.84(31)($\overline{1}0.0.8$), 3.402(100)($\overline{1}0.0.2$, $\overline{1}2.0.8$, 115), 3.369(74)($\overline{7}14$, 0.0.10), 2.815(70)(317, $\overline{1}1.1.4$), 2.756(36)(516, 12.0.3), 2.251(31)(1.1.12, 3.1.11), 2.116(31)($\overline{1}1.1.15$), 1.955(30)($\overline{1}9.1.5$, 11.1.8).

Crystal Structure

Data collection

Very few needles of rouxelite could be selected for a single-crystal X-ray study. Despite several attempts, only one among them gave usable data for a refinement of the structure. This crystal, elongated *b*, was mounted on a Nonius Kappa CCD diffractometer, using Mo$K\alpha$ radiation. Crystal data, data collection and structure refinement are given in Table 4. In all, 12099 reflections were measured to a maximum 2θ of 53.42°, and subsequently merged to 6329 independent reflections. This dataset was employed for structure solution; rouxelite has a monoclinic symmetry, space group $C2/m$, with unit-cell parameters as given in Table 4. The weak 2*b* superstructure could not be exploited in the dataset.

TABLE 2. RESULTS OF ELECTRON-PROBE MICRO-ANALYSIS OF ROUXELITE
FROM BUCA DELLA VENA AND MAGURKA

Anal., wt%	Cu	Ag	Hg	Pb	Sb	S	O**	Total	Anal., apfu	Cu	Ag	Hg	Pb	Sb	S	O**	Ev§
				Buca della Vena (sample 3780)									Buca della Vena (sample 3780)				
1	1.39	n.d.	1.69	45.11	31.50	20.16	0.55	100.40	1	2.29	-	0.88	22.77	27.06	65.76	3.60	-0.6
2	1.30	n.d.	1.81	45.09	31.61	20.14	0.35	100.30	2	2.14	-	0.94	22.76	27.15	65.69	2.29	-0.3
3	1.34	n.d.	1.85	45.08	31.71	20.12	0.46	100.56	3	2.20	-	0.96	22.68	27.16	65.42	3.00	0.1
4	1.41	n.d.	1.65	45.30	31.34	20.09	0.43	100.23	4	2.32	-	0.86	22.88	26.94	65.56	2.81	-0.4
5	1.28	n.d.	1.86	45.01	31.49	19.87	0.25	99.76	5	2.11	-	0.97	22.79	27.13	64.99	1.64	0.8
6	1.30	n.d.	1.69	44.84	31.37	20.01	0.30	99.51	6	2.16	-	0.89	22.81	27.15	65.76	1.98	-0.4
Mean	1.34	n.d.	1.76	45.08	31.50	20.07	0.39	100.13	Mean	2.20	-	0.92	22.78	27.10	65.53	2.55	-0.1
σ	0.05		0.09	0.15	0.14	0.11	0.11	0.40	σ	0.09	-	0.05	0.07	0.07	0.31	0.73	
Struct.*	1.22	-	1.92	44.86	31.94	19.86	0.20	100	Struct.*	2		1	22.61	27.39	64.67	1.33	-0.5
				Magurka (sample 47)									Magurka (sample 47)				
Mean (7)	1.28	0.35	1.07	45.59	31.94	19.92	n.d.	100.15	Mean (7)	2.08	0.33	0.55	22.80	27.24	64.38	-	+1.6
σ	0.16	0.05	0.10	1.34	0.25	0.15		1.31	σ	0.26	0.05	0.05	0.67	0.21	0.49	-	
			Ideal composition, $Cu_2HgPb_{22}Sb_{28}S_{64.67}O_{1.33}$									Ideal composition, $Cu_2HgPb_{22}Sb_{28}S_{64.67}O_{1.33}$					
	1.22	-	1.93	43.87	32.81	19.96	0.21	100		2	-	1	22	28	64.67	1.33	0

* According to the crystal-structure study; ** partly due to an oxidation-induced film (see text). § Ev: relative error (%) on the valence equilibrium. The proportions of atoms, expressed in atoms per formula unit (apfu), are calculated on the basis of ΣMe = 53 atoms; n.d.: not detected.
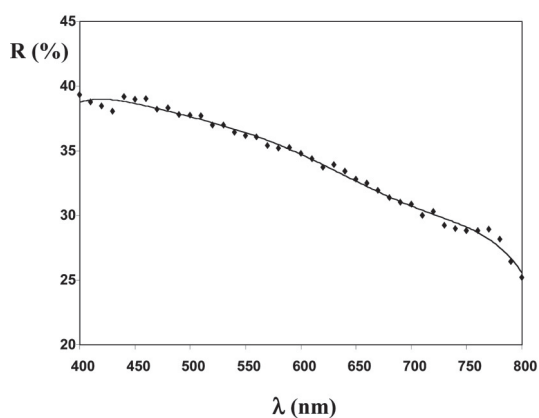

FIG. 2. Reflectance curve in air for a random section of rouxelite.

Structure determination

The structure of rouxelite was solved by means of direct methods and subsequent difference-Fourier syntheses. We made use of the SHELXTL program XL (crystal-structure refinement, version 6.12 Unix, 2001 Bruker–AXS). All final experimental data and refinement results are summarized in Table 4. The space group C2 was initially chosen, giving a final R value equal to 0.146, but as it induced asymmetric coordina- tion of some particular atoms [see the O(33),S(33) pair below], the space group C2/m was finally selected, despite a higher R value (0.169).

In Table 5, we give atom coordinates, site-occupancy factors and equivalent isotropic displacement parameters U(eq/iso), and in Table 6, we show anisotropic displacement parameters for cations (except for Cu). Among the cations, Cu and Hg positions are unique; there are nine Pb positions occupied by Pb, 12 Sb positions occupied by Sb [among which one, Sb(9), is split], one mixed (Pb,Sb)(13) position, and three Pb,Sb pairs (14, 15 and 16) corresponding each to two distinct positions within the same anionic polyhedron. In two of these three Pb,Sb pairs (14 and 15), the Sb position is split. There are 32 S positions, whereas another anion position has been resolved into an (O,S)(33) pair (see below).

For the mixed (Pb,Sb) position and the three Pb,Sb pairs, the Pb:Sb ratios have been refined with a constraint on the site-occupancy factors (s.o.f.; Table 5) such that the resulting number of atoms leads to four atoms, i.e., a fully occupied 4i site. These values are close to 0.78,0.22 for Pb(13),Sb(13), 0.50,0.50 for Pb(14),Sb(14), 0.57,0.43 for Pb(15),Sb(15), and 0.45,0.55 for Pb(16),Sb(16).

Special attention was given to anion position 33, close to Sb(2). Considering it as occupied entirely by S, i.e., with a s.o.f. equal to one, gave an excessively high B value; moreover, it gave also too short a S–Sb distance (below 2.2 Å). Conversely, considering it as a pure O atom also was inappropriate (the B value being

TABLE 3. POWDER X-RAY-DIFFRACTION PATTERN OF ROUXELITE

I_{meas}	d_{meas}	d_{calc}	I_{calc}	h	k	l
		10.5751	1	$\bar{4}$	0	1
16	10.400	10.4735	1	2	0	2
		9.8512	4	$\bar{4}$	0	3
10	8.08	8.1755	6	2	0	3
		7.5193	1	$\bar{2}$	0	5
		7.1313	3	$\bar{6}$	0	3
		6.8090	4	$\bar{6}$	0	4
		6.6557	4	2	0	4
6	5.91	5.8011	4	6	0	1
		4.2252	8	2	0	7
19	4.19	4.2049	7	0	0	8
		4.1809	10	$\bar{10}$	0	6
		4.1311	5	8	0	2
		4.0877	3	4	0	6
17	4.04	4.0364	4	1	1	0
		4.0335	8	$\bar{2}$	0	9
		4.0304	16	$\bar{10}$	0	7
		3.9571	4	$\bar{8}$	0	9
		3.9050	6	$\bar{3}$	1	1
		3.8899	7	$\bar{3}$	1	2
		3.8825	10	1	1	2
		3.8578	7	$\bar{1}$	1	3
31	3.84	3.8438	16	$\bar{10}$	0	8
		3.8292	4	10	0	0
		3.8146	7	8	0	3
		3.7835	13	3	1	1
10	3.76	3.7597	10	$\bar{4}$	0	10
		3.7377	3	0	0	9
		3.6724	3	$\bar{5}$	1	2
21	3.62	3.6376	10	$\bar{10}$	0	9
		3.6077	4	$\bar{2}$	0	10
		3.5894	17	$\bar{5}$	1	4
		3.5864	8	5	1	0
		3.5754	5	$\bar{3}$	1	5
		3.5721	6	1	1	4
		3.5377	10	$\bar{1}$	1	5
		3.5220	4	8	0	4
29	3.509	3.5011	27	$\bar{12}$	0	7
		3.4254	4	$\bar{10}$	0	10
		3.4138	3	$\bar{3}$	1	6
		3.4100	52	10	0	2
100	3.402	3.4045	31	$\bar{12}$	0	8
		3.4011	14	$\bar{4}$	0	11
		3.3896	23	1	1	5
		3.3887	3	$\bar{7}$	1	3
74	3.369	3.3657	15	$\bar{7}$	1	4
		3.3639	46	0	0	10
		3.3537	10	$\bar{1}$	1	6
		3.3107	12	$\bar{7}$	1	5
21	3.206	3.2030	9	1	1	6
		3.2017	13	10	0	3
		3.1673	4	$\bar{1}$	1	7
		3.1624	5	7	1	1
		3.1241	7	$\bar{7}$	1	7
		3.0950	7	$\bar{9}$	1	4
		3.0915	15	$\bar{9}$	1	3
		3.0749	3	$\bar{5}$	1	8
18	3.068	3.0693	4	5	1	4
		3.0624	7	$\bar{9}$	1	2
		3.0581	12	0	0	11
16	3.009	3.0107	3	$\bar{14}$	0	8
		3.0053	6	$\bar{7}$	1	8
		3.0032	8	10	0	4
		2.9949	24	1	1	6
		2.9442	9	$\bar{14}$	0	9
		2.9229	21	7	1	3
		2.9152	3	5	1	5
		2.9005	6	12	0	13
28	2.898	2.8970	21	$\bar{3}$	1	9
		2.8733	30	$\bar{9}$	1	8
		2.8439	9	1	1	8
		2.8271	23	3	2	0
70	2.815	2.8176	31	$\bar{11}$	1	4
		2.8164	8	$\bar{11}$	1	5
		2.8033	5	0	0	12
		2.7992	19	$\bar{11}$	1	3
		2.7957	3	$\bar{11}$	1	6
		2.7688	19	$\bar{5}$	1	10
		2.7633	13	5	1	6
		2.7624	4	$\bar{11}$	1	2
36	2.756	2.7567	6	$\bar{11}$	1	7
		2.7541	13	12	0	3
		2.7338	21	$\bar{3}$	1	10
		2.7022	3	$\bar{8}$	0	14
5	2.673	2.6716	12	$\bar{9}$	1	10
8	2.628	2.6337	8	$\bar{11}$	1	9
		2.6222	10	$\bar{8}$	1	11
		2.5639	4	$\bar{13}$	1	6
15	1.871	2.5312	6	$\bar{13}$	1	3
9	2.528	2.4811	4	11	1	2
5	2.481	2.3855	2	$\bar{18}$	0	6
		2.3840	1	13	1	0
6	2.385	2.3816	2	$\bar{11}$	1	12
12	2.350	2.3456	6	$\bar{15}$	1	6
		2.3406	8	$\bar{15}$	1	7
5	2.309	2.3096	6	$\bar{12}$	0	16
		2.2572	7	$\bar{15}$	1	2
		2.2519	11	1	1	12
31	2.251	2.2513	10	3	1	11
		2.2403	16	$\bar{9}$	1	14
16	2.220	2.2186	8	6	0	12
		2.2123	5	$\bar{15}$	1	1
19	2.150	2.1506	7	$\bar{20}$	0	7
		2.1451	3	$\bar{17}$	1	8
		2.1369	3	$\bar{20}$	0	6
		2.1218	9	11	1	6
31	2.116	2.1156	3	$\bar{17}$	1	4
		2.1136	4	9	1	8
		2.1113	22	$\bar{11}$	1	15
16	2.089	2.0881	10	$\bar{17}$	1	3
		2.0872	5	6	0	13
		2.0832	7	$\bar{12}$	0	18
		2.0538	5	$\bar{17}$	1	2
21	2.042	2.0351	11	11	1	7
		2.0295	59	0	2	0
		1.9934	3	$\bar{10}$	0	19
13	1.983	1.9834	2	15	1	3
		1.9802	2	$\bar{19}$	1	8
		1.9791	3	$\bar{19}$	1	7
		1.9765	3	7	1	11
		1.9566	7	$\bar{19}$	1	5
30	1.955	1.9530	3	$\bar{9}$	1	17
		1.9516	9	11	1	8
		1.9480	3	$\bar{22}$	0	7
11	1.923	1.9217	3	17	1	1
		1.9213	2	1	1	15
		1.9206	4	15	1	4
		1.9192	4	$\bar{19}$	1	12
		1.9010	4	$\bar{16}$	0	19
		1.8932	4	$\bar{10}$	0	20
15	1.888	1.8863	6	10	0	12
15	1.871	1.8711	4	$\bar{20}$	0	17
		1.8677	4	$\bar{9}$	1	18
		1.8646	7	$\bar{15}$	1	17
		1.8287	7	1	1	16
		1.8185	6	$\bar{19}$	1	15
15	1.814	1.8118	12	$\bar{1}$	1	17
		1.8057	3	13	1	8
		1.8008	4	7	1	13
		1.7959	4	11	1	10
		1.7952	5	10	0	13
		1.7947	5	$\bar{10}$	2	8
9	1.780	1.7799	3	$\bar{21}$	1	4
		1.7788	6	$\bar{21}$	1	13
		1.7558	7	$\bar{12}$	2	7
		1.7440	17	10	2	2
26	1.743	1.7433	8	$\bar{12}$	2	8
		1.7428	4	$\bar{4}$	2	11
		1.7377	13	0	2	10
		1.7282	5	$\bar{24}$	0	15
		1.7141	4	10	2	3
16	1.704	1.7050	7	20	0	4
		1.7005	4	$\bar{8}$	0	22
		1.6910	5	0	2	11
7	1.681	1.6820	4	0	0	20
		1.6710	4	$\bar{14}$	2	9
		1.6610	4	$\bar{2}$	0	21
		1.6338	4	12	2	3

not indexed

I_{meas}	d_{meas}
5	1.573
6	1.506
15	1.473
5	1.438
22	1.415
12	1.400
14	1.383
22	1.345

Operating conditions: Gandolfi camera (114.6 mm in diameter); Cu$K\alpha$ radiation (40 kV, 20 mA).

too low). Thus this anion position was split into an O(33),S(33) pair, with a total s.o.f. of 1 (a total s.o.f. of 0.50 was insufficient). The O:S ratio was then adjusted in order to give a B value in accordance with those of the other S atoms; the O:S ratio was thus fixed at 2:1, which must be considered as a first approximation, owing to the poor quality of the crystal studied.

The empirical formula resulting from this crystal-structure study is $Cu_2HgPb_{22.6}Sb_{27.4}S_{64.67}O_{1.33}$. According to this structural model, with a total of 33 anions in the structural formula, one ought to have 22 Pb and 28 Sb atoms in addition to 1 Hg and 2 Cu atoms to respect electrostatic neutrality. On the other hand, the Pb:Sb ratio given by EPMA is close to 23:27. This discrepancy could not be resolved, and is probably related to the insufficient quality of the resolution of the crystal structure. In spite of this, the structural model seems new and unique, and it can clearly be described according to the general principles of modular analysis developed by Makovicky (1981, 1985) for lead sulfo-salts and related compounds.

Description of the structure

Figure 3 presents the projection of the unit cell along b. Owing to the complexity of the structure (and the
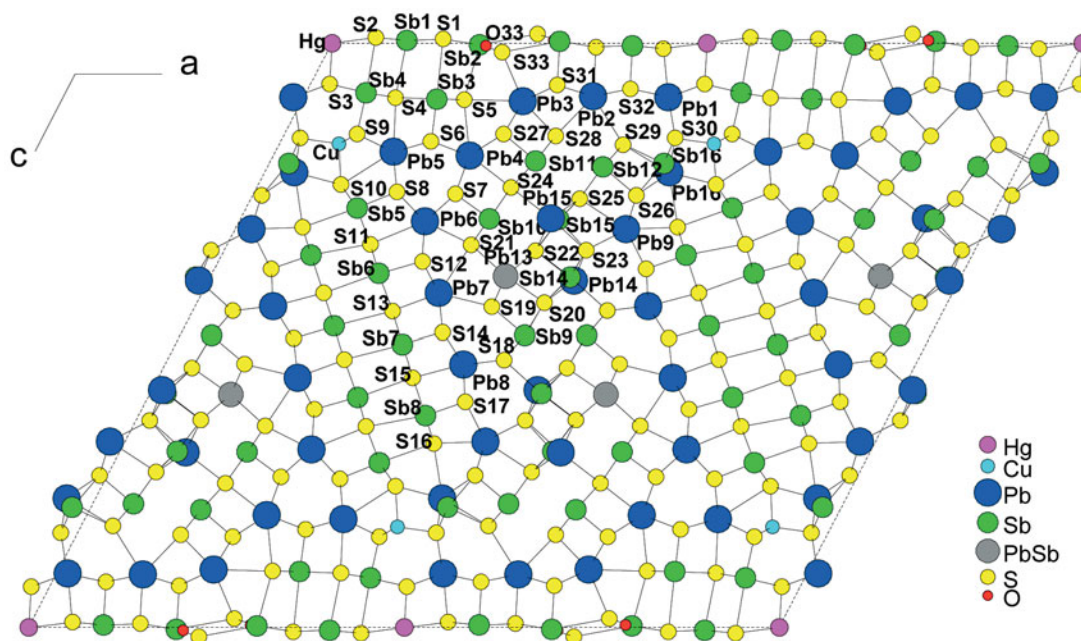
Fig. 3. Projection of the crystal structure of rouxelite along *b*.

TABLE 4. DATA ON THE CRYSTAL OF ROUXELITE
AND ON THE STRUCTURE REFINEMENT

Crystal Data

Empirical formula	$Cu_2HgPb_{22.6}Sb_{27.4}S_{64.67}O_{1.33}$
Formula weight	10441.8
Crystal system	monoclinic
Space group	$C2/m$ (#12)
a	43.113(9) Å
b	4.0591(8) Å
c	37.874(8) Å
β	117.35 (3)°
V	5887(2) Å³
Z	2
Density (calculated)	5.891 g/cm³

Data Collection

Temperature	293(2) K
Size of the crystal (mm)	$0.04 \times 0.30 \times 0.04$
Radiation	Mo$K\alpha$ ($\lambda = 0.71073$ Å)
	60 kV x 35 mA
Diffractometer	Nonius Kappa CCD
θ range	1.45 to 26.71°
Reflections collected	12099
Independent reflections	6329 [R(int) = 0.1141]
Index ranges	$-46 \leq h \leq 54, -5 \leq k \leq 4, -41 \leq l \leq 47$

Refinement

Refinement method	Full-matrix least-squares on F²
Data/restraints/parameters	6326/0/266
Goodness-of-fit on F²	2.971
R1 [for 4780 reflections with I ≥ 2σ(I)]	0.1686
R1 index (for all 6326 reflections)	0.2016
Largest diffraction peak,hole	7.53, −6.15 e .Å³

poor *R* value), only the coordination of some specific atoms will be discussed. The Hg atom presents a classic case of a distorted octahedral coordination (Fig. 4), with two short opposite bonds with S(3) (2.381 Å: Table 7), and four long equatorial ones with S(2) (3.267 Å × 4). The bond-valence sum (BVS), according to Brese & O'Keeffe (1991), is equal to 2.02 valence units (*vu*). In cinnabar (trigonal α-HgS), there are two apical bonds at 2.377 Å, and four equatorial ones at 3.093 Å (×2) and 3.279 Å (×2). Other examples of such a coordination in two Hg sulfosalts, livingstonite (Niizeki & Buerger 1957) and grumiplucite (Mumme & Watts 1980), are given in Table 7 (Hg–S distances and S–Hg–S angles).

The Cu atom has a tetrahedral coordination (Fig. 4), with S atoms at 2.245, 2.398 and two at 2.345 Å, and a BVS equal to 1.12 *vu*. This tetrahedron is relatively regular, with S–Cu–S angles between 100 and 120°.

The O(33),S(33) pair is presented in Figure 5. Atom O(33) is coordinated to two Sb(2) atoms at 2.052 Å ($BVS_{O(33)} = 1.62$ *vu*); the Sb(2)–O(33)–Sb(2) angle is 162.9°. Atom S(33) is coordinated to two Sb(2) at 2.468 Å [Sb(2)–S(33)–Sb(2) = 110.6°], another Sb(2) atom at 3.430 Å, and two Pb(3) atoms at 3.602 Å ($BVS_{S(33)}$ = 2.09 *vu*).

The main structural features of the crystal structure of rouxelite are represented in Figure 6. There are CuS_4 and HgS_6 polyhedra, local triangular arrangements of atoms around a pseudotrigonal axis (red triangles), flat-

tened ellipses (green) representing the micelles between Sb atoms, into which are directed their lone pairs of electrons, and one-atom-thick walls of S atoms (brown tie-lines) separating structural subunits, as explained below.

Modular analysis of the crystal structure

According to our modular analysis, the crystal structure of rouxelite can easily be related to the boxwork type of lead sulfosalts, as has been exemplified initially for the crystal structure of neyite, $Ag_2Cu_6Pb_{25}Bi_{26}S_{68}$ (Makovicky *et al.* 2001). This boxwork organization is obtained by combination of three PbS- or SnS-type modules (Fig. 7). Firstly, there is an alternation along *a* of two types of ribbons (elongation parallel to *b*),

one (denoted Q) corresponding to a (100) section of the PbS archetype (pseudotetragonal Q-type ribbon), four atom-layers thick, five octahedra wide, with a composition $Cu_2Pb_{10}(Pb,Sb)_2Sb_{10}S_{26}$, the second one (denoted H) corresponding to a (120) section of SnS (pseudohexagonal H-type ribbon; Del Bucchia *et al.* 1981), five atom-layers (= two pseudo-octahedra) thick, seven (pseudo)octahedra wide, with a composition $Pb_2(Pb,Sb)_6Sb_6S_{24}$. The H-type ribbon can be considered as a SnS-type distortion of the hexagonal layer in tetradymite. These Q and H ribbons alternate along *a* to form a complex slab parallel to (001). Secondly, along *c*, two consecutive slabs are separated by a three-atom-thick layer (noted L in Fig. 7; see also Fig. 8a), derived from (100)$_{PbS}$. This layer can be considered as the succession along *a* of ribbons centered on the

TABLE 5. CRYSTAL STRUCTURE OF ROUXELITE: SITE-OCCUPANCY FACTORS, ATOM COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS

Atom	s.o.f	x	y	z	U(eq/iso)	Atom	s.o.f	x	y	z	U(eq/iso)
Hg	1	0	0	0	0.032(1)	S(3)	1	0.0247(6)	0	0.0706(6)	0.022(5)
Cu	1	0.0792(3)	0	0.1719(3)	0.030(3)	S(4)	1	0.1223(6)	0	0.0930(7)	0.030(6)
Pb(1)	1	0.4860(1)	0	0.0926(1)	0.029(1)	S(5)	1	0.2145(6)	0	0.0962(7)	0.029(5)
Pb(2)	1	0.3853(1)	0	0.0914(1)	0.028(1)	S(6)	1	0.1994(7)	½	0.167(7)	0.033(6)
Pb(3)	1	0.2942(1)	0	0.0992(1)	0.034(1)	S(7)	1	0.2687(5)	½	0.2582(6)	0.018(5)
Pb(4)	1	0.2607(1)	0	0.1923(1)	0.033(1)	S(8)	1	0.1881(5)	½	0.2543(6)	0.013(4)
Pb(5)	1	0.1566(1)	0	0.1858(1)	0.035(1)	S(9)	1	0.0981(6)	½	0.1573(7)	0.030(6)
Pb(6)	1	0.2466(1)	0	0.3051(1)	0.035(1)	S(10)	1	0.1101(7)	0	0.2432(8)	0.036(6)
Pb(7)	1	0.3149(1)	0	0.4278(1)	0.029(1)	S(11)	1	0.1900(8)	0	0.3435(8)	0.045(7)
Pb(8)	1	0.3968(1)	0	0.5500(1)	0.033(1)	S(12)	1	0.2701(5)	½	0.3738(6)	0.016(4)
Pb(9)	1	0.5208(1)	0	0.3187(1)	0.034(1)	S(13)	1	0.2643(7)	0	0.4573(8)	0.037(6)
Sb(1)	1	0.0977(2)	0	-0.0045(2)	0.028(2)	S(14)	1	0.3469(7)	½	0.4939(7)	0.032(6)
Sb(2)	1	0.1971(2)	0	0.0028(2)	0.033(2)	S(15)	1	0.3386(7)	0	0.5728(8)	0.038(6)
Sb(3)	1	0.1779(2)	½	0.0957(2)	0.026(1)	S(16)	1	0.4114(7)	0	0.6853(8)	0.035(6)
Sb(4)	1	0.0799(2)	½	0.0851(2)	0.030(2)	S(17)	1	0.4255(6)	½	0.6138(6)	0.023(5)
Sb(5)	1	0.1473(2)	½	0.2825(2)	0.032(2)	S(18)	1	0.4487(8)	½	0.5414(9)	0.046(7)
Sb(6)	1	0.2213(1)	½	0.3940(2)	0.021(1)	S(19)	1	0.3959(7)	0	0.4512(8)	0.041(7)
Sb(7)	1	0.3021(2)	½	0.5162(3)	0.044(2)	S(20)	1	0.4616(6)	½	0.4444(6)	0.020(5)
Sb(8)	1	0.3816(2)	½	0.6377(2)	0.034(2)	S(21)	1	0.3241(6)	0	0.3452(7)	0.031(6)
Sb(9)	0.5	0.4584(2)	0.083(2)	0.4991(3)	0.037(4)	S(22)	1	0.4141(7)	0	0.3554(7)	0.034(6)
Sb(10)	1	0.3309(2)	½	0.3008(3)	0.059(2)	S(23)	1	0.4820(7)	½	0.3549(8)	0.038(6)
Sb(11)	1	0.3526(2)	½	0.2019(3)	0.052(2)	S(24)	1	0.3384(7)	0	0.2471(8)	0.038(6)
Sb(12)	1	0.4466(2)	½	0.2121(2)	0.041(2)	S(25)	1	0.4375(9)	0	0.2666(9)	0.054(8)
Pb(13)	0.78(2)	0.3925(1)	½	0.3991(2)	0.050(2)	S(26)	1	0.5113(6)	½	0.2607(7)	0.028(5)
Sb(13)	0.22(2)	0.3925(2)	½	0.3991(-)	0.050(2)	S(27)	1	0.2915(6)	½	0.1551(7)	0.024(5)
Pb(14)	0.50(2)	0.4827(4)	0	0.4031(4)	0.047(3)	S(28)	1	0.3623(6)	0	0.1592(7)	0.027(5)
Sb(14)	0.25(2)	0.4778(8)	0.112(10)	0.4002(9)	0.047(3)	S(29)	1	0.4577(7)	0	0.1738(7)	0.035(6)
Pb(15)	0.574(15)	0.4145(4)	½	0.3003(3)	0.045(3)	S(30)	1	0.5240(7)	½	0.1629(7)	0.031(6)
Sb(15)	0.213(15)	0.4270(9)	0.467(13)	0.3020(7)	0.045(3)	S(31)	1	0.3292(6)	½	0.0719(6)	0.022(5)
Pb(16)	0.452(7)	0.5394(3)	0	0.2216(3)	0.023(2)	S(32)	1	0.4298(6)	½	0.0776(6)	0.021(5)
Sb(16)	0.548(7)	0.5258(4)	0	0.2058(5)	0.023(2)	S(33)	⅓	0.234(2)	½	0.018(2)	0.034(14)
S(1)	1	0.1459(9)	½	-0.0057(10)	0.059(9)	O(33)	⅔	0.205(3)	½	0.006(3)	0.034(14)
S(2)	1	0.0557(7)	½	-0.0083(8)	0.042(7)						

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. U(eq/iso) values are expressed in Å²; s.o.f.: site-occupancy factor.
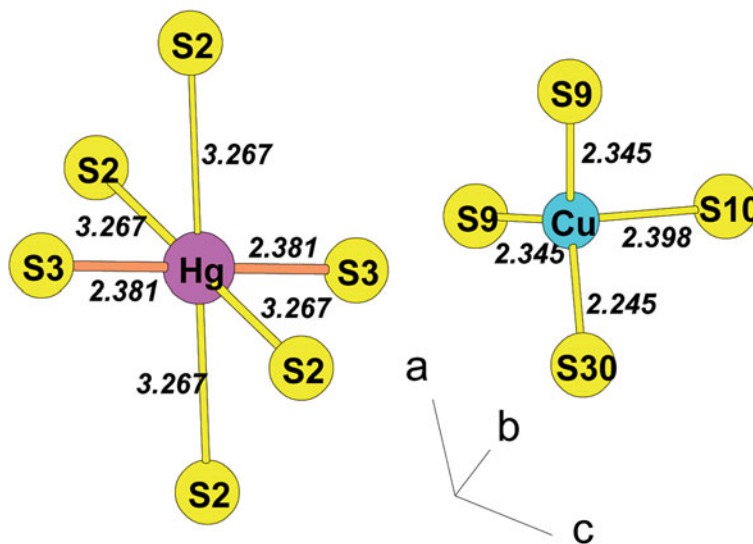
Fig. 4.   Coordination of Hg and Cu in the crystal structure of rouxelite.

Hg atoms, and separated by the oxygen atoms, with the composition $[HgPb_6Sb_8S_{14}(O,S)_2]$. Two consecutive ribbons are related by a $b/2$ shift. Thus, the final structural formula is: $[Cu_2Pb_{10}(Pb,Sb)_2Sb_{10}S_{26}] + [Pb_2(Pb,Sb)_6Sb_6S_{24}] + [HgPb_6Sb_8S_{14}(O,S)_2] = Cu_2Hg Pb_{18}(Pb,Sb)_8Sb_{24}S_{64}(O,S)_2$.

There are close relationships with the three building blocks described in neyite (Makovicky *et al*. 2001). Firstly, the Q-type ribbon is two-atom-thick layers in neyite, but four-atom-thick layers in rouxelite, whereas the H-type ribbon is three octahedra thick in neyite, and only two (pseudo)octahedra thick in rouxelite. In neyite, the two ribbons are stepped, with intercalation of copper at the center of the Q-type ribbon. The alternation of these two types of ribbons is a finite derivation from the composite layered structure of cannizzarite (Matzat 1979, Makovicky & Hyde 1981). Secondly, in neyite, the ribbon-layer (Fig. 8b) is topologically very close to the ribbon-layer of the $(100)_{PbS}$ type in the synthetic compound $Pb_3In_{6.67}S_{13}$ (Fig. 8c; Ginderow 1978, Makovicky 1981). Its ribbon formula is $AgPb_6Bi_6S_{14}$, to be compared with formula $Pb_{5.33}In_7S_{14}$ for the ribbon of the Pb,In sulfide. These ribbon-layers are sheared, so that in neyite, two successive ribbons show a one-atom-plane shift in the (a, c) projection (Fig. 8b). In rouxelite (Fig. 8a), one recognizes the same type of ribbon, with the addition of two Pb and (O,S) atoms at the connection between two consecutive ribbons, and a $b/2$ shift; the unit formula of the ribbon-layer is thus $HgPb_6Sb_8S_{14}(O,S)_2$.

The Hg and Ag atoms in rouxelite and neyite, respectively, present quite the same environment at the center of their respective ribbon. In particular, they
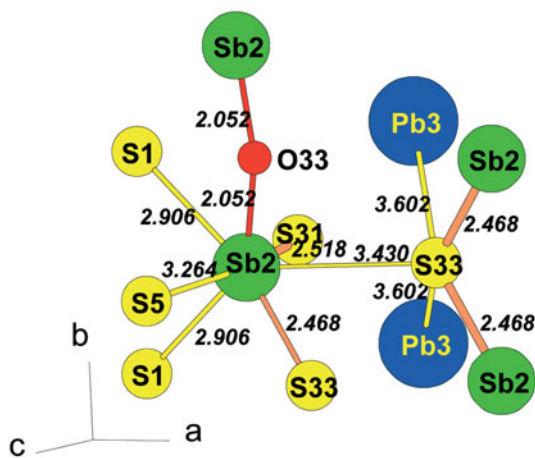
Fig. 5.   Coordination of the O(33),S(33) pair in the crystal structure of rouxelite. For clarity, only one O or S position has been selected.

have the same coordination, with similar (Hg,Ag)–S bond lengths and S–(Hg,Ag)–S angles (Table 7). This steric similarity leads us to suggest that in rouxelite from Magurka, the minor Ag content substitutes for Hg at the same site, according to the substitution $Hg^{2+} \rightarrow Ag^+$, probably compensated by the substitution $Pb^{2+} \rightarrow Sb^{3+}$ at an adjacent site. The substitution is pronounced, as the Ag:Hg atom ratio is close to 0.60, and the extent of the solid solution toward (and possibly up to) the

pure Ag end-member, which would correspond to a distinct mineral species, appears very probable. Such a Hg-free end-member would have the ideal composition $Cu_2AgPb_{21}Sb_{29}S_{64}(O,S)_2$.

The rouxelite and neyite structures, organized on the basis of three types of ribbons, can thus be defined as three-component structures of the boxwork type derived from the cannizzarite layered two-component type. On the basis of the hierarchical classification developed by Makovicky (1997), they correspond to a plesiotypic pair. According to one of their two modular descriptions, the crystal structures of pillaite (Meerschaut *et al.* 2001) and pellouxite (Palvadeau *et al.* 2004) can also be considered as members of the same boxwork type. The crystal structure of $Er_9La_{10}S_{27}$ (Carré & Laruelle 1973) has been described by Makovicky (1992) as another example of boxwork structure with the alternation along *a* of two-atom-layers thick PbS/SnS ribbons with one-octahedron thick CdI_2-type ribbons. These ribbon sequences are separated along *c* by ribbon-layers (with the ribbons three-octahedra wide: Fig. 8d) homologous to those of $Pb_3In_{6.67}S_{13}$ (ribbons four octahedra wide).

This boxwork description is one of the possible modular interpretations; it neglects some strong bonds between the three modules. Complementary to this description, the structural characters linking rouxelite to so-called cyclically organized sulfosalt structures (Makovicky 1985) need to be emphasized. The Pb atoms 4, 5 and 6 (Fig. 3) form a pseudotrigonal column (Fig. 9a) at the triple junction between two ribbons H and Q and a rod-layer L. The Pb atoms 8 and 9 and the Pb(14),Sb(14) pair form a similar but less regular configuration, as one side of the pseudotriangular column is lacking. Such pseudotrigonal columns are

characteristic of sulfosalts of the zinkenite family (Makovicky 1985); here they are directly derived from hexagonal $Ba_{12}Bi_{24}S_{48}$ (Aurivillius 1983). At a larger scale, such a connection is very similar to a large fragment of the crystal structure of a member of the zinkenite family, kobellite (Miehe 1971).

In Figures 9a and 9b, one can visualize the paving of the projections of the crystal structures of rouxelite and kobellite using the same type of tiles *T* (*i.e.*, outlines of complex columns). With this illustration, one can cover the entire projection of the crystal structure of rouxelite, except for a residual M_4S_4 interstice *R* among four tiles (Fig. 9a: *M* represents all cations except Cu). The same approach applies to the projection of the crystal structure of kobellite, except for a residual $Cu_2(M_{1/2})_2M_4S_7(S_{1/2})_2$ interstice *R'* between six tiles (Fig. 9b) (We note that here and below, atoms with ½ as subscript are at the junction between 2 *T*, or between *T* and *R* or *R'*). In the two cases, there is one residual ribbon *R* or *R'* for two tiles *T*, and the crystal formulas can be written as R (or R') + 2 *T*. In rouxelite, *T* stands for $CuHg_{1/2}Pb_9(Pb/Sb)_3(Sb_{1/2})_4Sb_9S_{28}(S_{1/2})_4[(O,S)_{1/2}]_2 = CuM_{23.5}An_{31}$ (An:

TABLE 7. (Hg,Ag)–S DISTANCES, BOND VALENCES AND S–(Hg,Ag)–S ANGLES IN ROUXELITE, NEYITE, LIVINGSTONITE AND GRUMIPLUCITE

	d (Å)	B. V.		d (Å)	B. V.	(Hg)*
Rouxelite			**Neyite**			
Hg -S(3) × 2	2.381	0.85 × 2	Ag -S(22) × 2	2.415	0.49	(0.77) × 2
-S(2) × 4	3.267	0.08 × 4	-S(18) × 4	3.139	0.07	(0.11) × 4
Sum		2.02	Sum		1.26	(1.98)
Angles:						
S(2)-Hg-S(3)	82.04°		S(22)-Ag-S(18)	82.02°		
«	97.96°		«	97.98°		
S(2)-Hg-S(2)	76.82°		S(18)-Ag-S(18)	80.85°		
«	103.1°		«	99.15°		
Livingstonite						
Hg(1)-S(2) × 2	2.368	0.88 × 2	Hg(2)-S(7) × 2	2.364	0.89 × 2	
-S(3) × 2	3.345	0.06 × 2	-S(6) × 2	3.341	0.06 × 2	
-S(3) × 2	3.378	0.06 × 2	-S(6) × 2	3.364	0.06 × 2	
Sum		2.00	Sum		2.02	
Angles:						
S(2)-Hg-S(3)	75.12°		S(7)-Hg-S(6)	75.64°		
«	76.10°		«	76.57°		
«	103.90°		«	103.53°		
«	104.88°		«	104.27°		
S(3)-Hg-S(3)	73.02°		S(6)-Hg-S(6)	73.25°		
«	106.98°		«	73.25°		
«	73.02°		«	106.20°		
«	106.98°		«	107.30°		
Grumiplucite						
Hg(1)-S(2) × 2	2.386	0.84 × 2	Hg(2)-S(4) × 2	2.409	0.79 × 2	
-S(1) × 4	3.102	0.12 × 4	-S(3) × 4	3.150	0.11 × 4	
Sum		2.16	Sum		2.02	
Angles:						
S(2)-Hg-S(1)	83.48°		S(4)-Hg-S(3)	86.61°		
«	96.52°		«	93.32°		
S(1)-Hg-S(1)	81.76°		S(3)-Hg-S(3)	80.24°		
«	98.24°		«	99.76°		

B.V.: Bond valence calculated according to Brese & O'Keeffe (1991). *: B.V. if Hg were to substitute for Ag in neyite.

TABLE 6. ANISOTROPIC DISPLACEMENT PARAMETERS (Å²) FOR CATIONS IN THE CRYSTAL STRUCTURE OF ROUXELITE

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	0.036(3)	0.031(3)	0.029(3)	0	0.013(2)	0
Pb(1)	0.030(2)	0.020(2)	0.034(2)	0	0.012(2)	0
Pb(2)	0.026(2)	0.022(2)	0.036(2)	0	0.014(2)	0
Pb(3)	0.040(2)	0.029(2)	0.034(2)	0	0.018(2)	0
Pb(4)	0.032(2)	0.025(2)	0.048(2)	0	0.023(2)	0
Pb(5)	0.028(2)	0.037(2)	0.040(2)	0	0.014(2)	0
Pb(6)	0.036(2)	0.029(2)	0.038(2)	0	0.015(2)	0
Pb(7)	0.025(2)	0.028(2)	0.036(2)	0	0.015(2)	0
Pb(8)	0.025(2)	0.036(2)	0.038(2)	0	0.015(2)	0
Pb(9)	0.042(2)	0.030(2)	0.037(2)	0	0.023(2)	0
Sb(1)	0.021(3)	0.033(4)	0.027(3)	0	0.009(3)	0
Sb(2)	0.035(4)	0.028(4)	0.032(4)	0	0.011(3)	0
Sb(3)	0.029(4)	0.027(4)	0.022(3)	0	0.010(3)	0
Sb(4)	0.030(4)	0.030(4)	0.031(4)	0	0.014(3)	0
Sb(5)	0.024(3)	0.053(5)	0.020(3)	0	0.010(3)	0
Sb(6)	0.011(3)	0.022(3)	0.032(3)	0	0.011(2)	0
Sb(7)	0.046(5)	0.030(4)	0.081(6)	0	0.049(4)	0
Sb(8)	0.034(4)	0.040(4)	0.036(4)	0	0.023(3)	0
Sb(9)	0.029(4)	0.040(11)	0.040(5)	-0.010(4)	0.015(4)	-0.003(4)
Sb(10)	0.024(4)	0.044(5)	0.084(6)	0	0.004(4)	0
Sb(11)	0.034(4)	0.034(4)	0.064(5)	0	0.001(4)	0
Sb(12)	0.029(4)	0.058(5)	0.034(4)	0	0.013(3)	0
Pb,Sb(13)	0.042(3)	0.059(4)	0.060(4)	0	0.032(3)	0

anions), R stands for $(Pb,Sb)_2Sb_2S_4 = M_4An_4$, and the sum $2 T + R$ is equal to $Cu_2M_{51}An_{66}$. In tintinaite, the Fe- and Bi-free isotype of kobellite (Moëlo et $al.$ 1984, 1995), T stands for $CuPb_{11}Sb_{10}(Sb_{1/2})_5S_{28}(S_{1/2})_6 = CuM_{23.5}An_{31}$, R' stands for $Cu_2Pb_2Sb_2(Sb_{1/2})_2S_7(S_{1/2})_2 = Cu_2M_5An_8$, and the sum $2 T + R' = Cu_4M_{52}S_{70}$.

From a topological point of view, the percentages of equivalent positions in each structure corresponds to one hundred times the atomic ratio $[2 T / (2T + R)]$ $= 100•111/119 = 93.3\%$ for rouxelite, and $100 [2 T/(2 T + R')] = 100•111/126 = 88.1\%$ for tintinaite and kobellite.

The alternation of tiles along [110] of kobellite is broadly similar to this alternation along a in rouxelite, giving close periodicities (40.90 Å $versus$ 43.113 Å). As a corollary, the unit-cell volumes also are close (5887 Å³ for rouxelite $versus$ $3098 \times 2 = 6198$ Å³ for the tintinaite chemically closest to kobellite).

Choi et $al.$ (2001) have described five compounds with the general formula $A_{1+x}M_{4-2x}M'_{7+x}Se_{15}$ (A = K,

Rb; M = Pb, Sn; M' = Bi, Sb). Their crystal structures are all based on the combination of stepped H-type layers, two-octahedra thick, with Q-type rods, four-atom-layers thick. Such an identical stacking gives closer c periodicities (between 21.64 and 21.75 Å), to be compared with the a periodicity of 43.11 Å (= 2 × 21.56 Å) in rouxelite. Rouxelite can thus be considered as a higher structural derivative of that family, and to be of the boxwork type.

DISCUSSION

This mineralogical and structural study of rouxelite contributes to three more general scientific aspects.

Systematics of Hg sulfosalts

In the three new lead sulfosalts earlier discovered at Buca della Vena, the critical chemical factor controlling
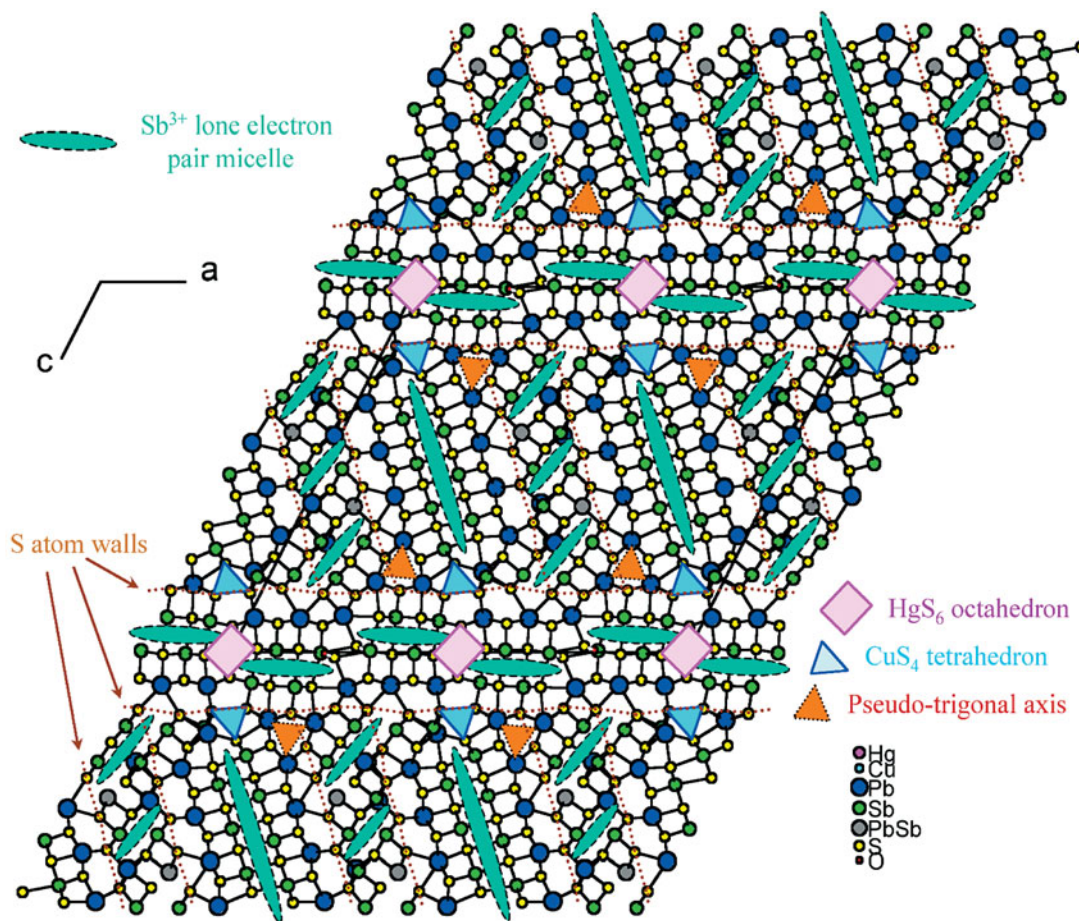
FIG. 6.   The main structural features of the crystal structure of rouxelite.

their formation is the presence of one or two additional anions, oxygen and chlorine, plus minor Cu (with Ag) for one of them (pellouxite). For rouxelite, minor copper and oxygen are present as well, but another critical chemical factor is the presence of minor mercury. There are few sulfosalts having mercury as a specific constituent chemical element (Strunz & Nickel 2001): 1) sulfosalts of Hg: grumiplucite, $HgBi_2S_4$, livingstonite, $HgSb_4S_8$, and tvalchrelidzeite, Hg_3SbAsS_3, 2) Hg–Tl sulfosalts: vaughanite, $HgTlSb_4S_7$, vrbaite, $Hg_3Tl_4As_8Sb_2S_{20}$, simonite, $HgTlAs_3S_6$ and christite, $HgTlAsS_3$, 3) (Cu,Ag)–Hg sulfosalts: aktashite, $Cu_6Hg_3As_4S_{12}$, laffittite, $AgHgAsS_3$ and fettelite, $Ag_{24}HgAs_5S_{20}$, and 4) complex sulfosalts: petrovicite, $Cu_3HgPbBiSe_5$ (a seleniosalt), routhierite, $CuHg_2TlAs_2S_6$, and galkhaite, $(Cs,Tl,\square)(Hg,Cu,Zn,Tl)_6(As,Sb)_4S_{12}$. Rouxelite can be added to this last subgroup.

Rouxelite formation and the regional metallogeny of Hg

At Buca della Vena, the rarity of rouxelite reflects the geochemical scarcity of mercury relative to Pb and Sb, and also to Cu. At a regional scale, this is in accordance with the distribution of mercury deposits in Tuscany. These deposits are located essentially in the southern part, principally close to the trachyte intrusive body of Monte Amiata (Dessau 1977). In the northern part of Tuscany, within the Apuan Alps, mercury occurrences are rare (Lattanzi *et al*. 1994, Dini *et al*. 2001). There are only two small Hg deposits, Levigliani (3 km northwest of Buca della Vena) and Ripa (7 km west) (Carmignani *et al*. 1972). Whereas the only Hg mineral is cinnabar at Ripa, this sulfide is accompanied by minor metacinnabar, native mercury, mercurian sphalerite (Dini *et al*. 1995), and traces of grumiplucite, $HgBi_2S_4$
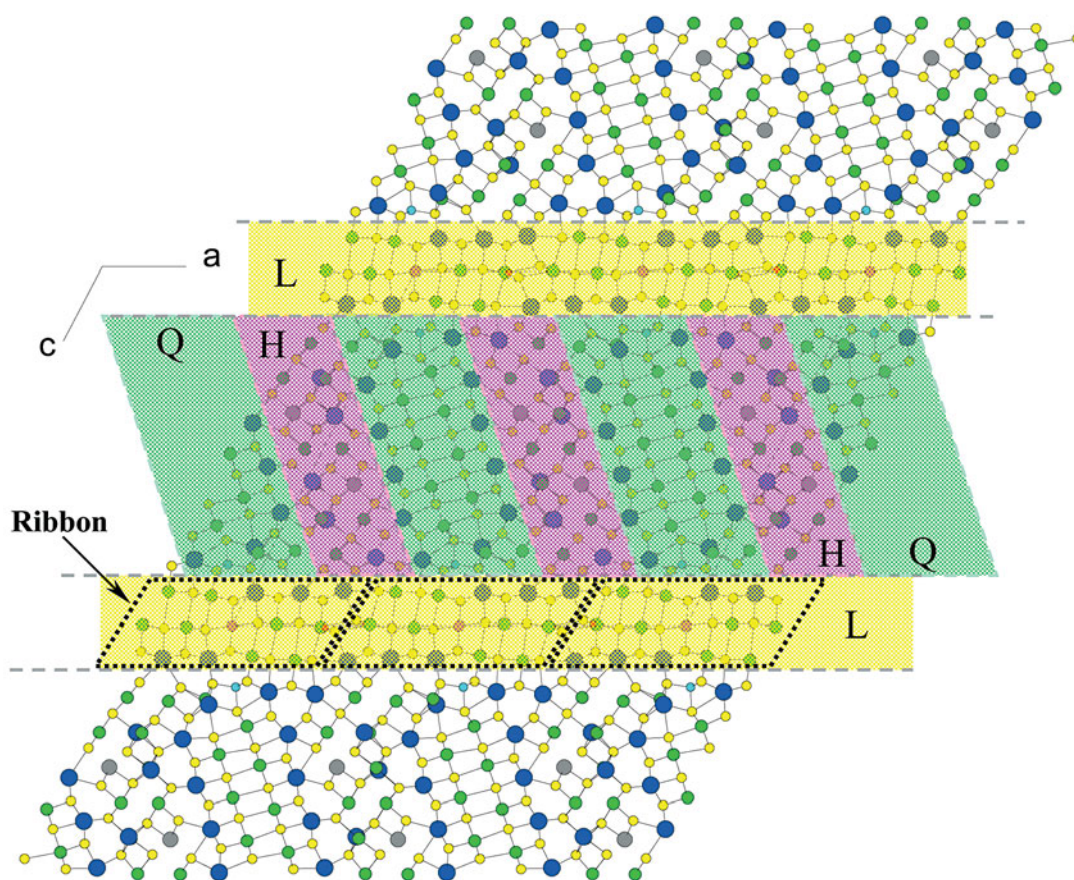
FIG. 7.   Boxwork architecture of the crystal structure of rouxelite. Q: pseudotetragonal ribbons (green), H: pseudohexagonal ribbons (pink), L: ribbon-layer (yellow: constitutive ribbons, dashed outlines).
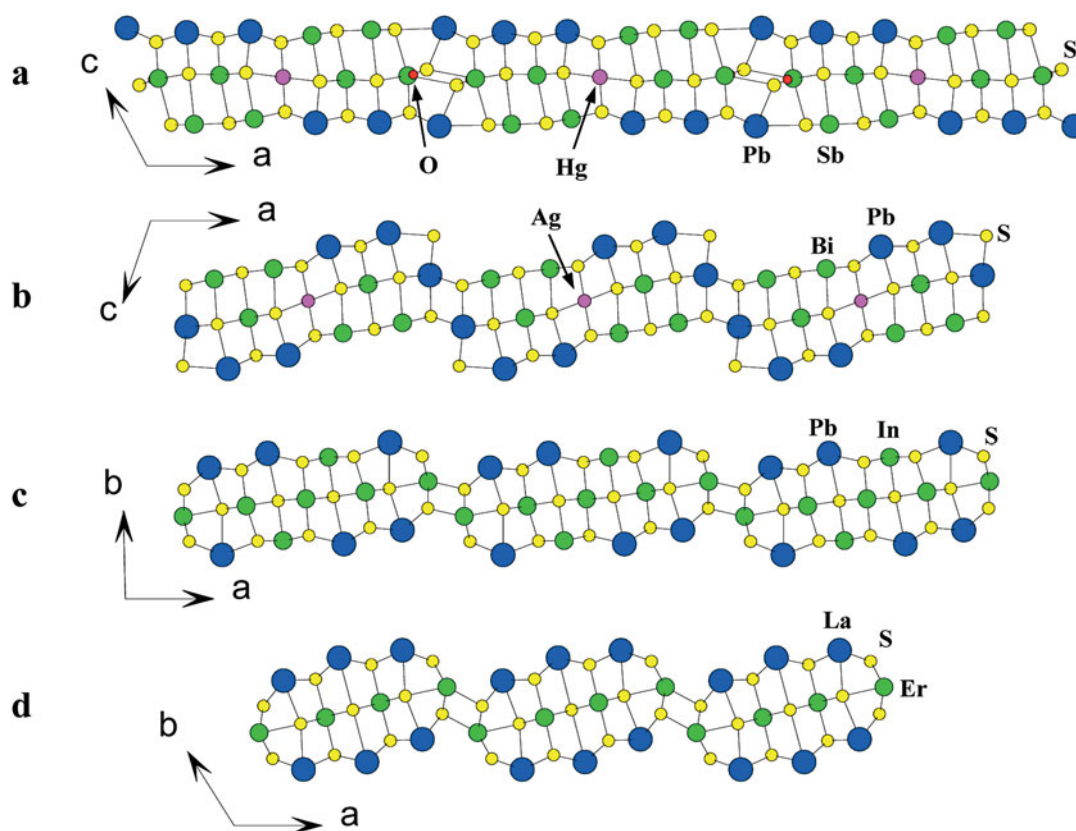
FIG. 8.   Comparison of the three-atom-thick ribbon-layers of rouxelite (a), neyite (b), $Pb_3In_{6.67}S_{13}$ (c), and $Er_9La_{10}S_{27}$ (d).

(Orlandi *et al*. 1998) at Levigliani. In addition to Buca della Vena, traces of cinnabar are known at the Pollone Ba–Fe deposit, at the Bottino Pb deposit, and within the cavities of the Apuan Alps marble (Orlandi & Bellè 2002). Costagliola *et al*. (1990) indicated the presence of polhemusite, (Zn,Hg)S, at Monte Arsiccio, another Ba–Fe deposit. Finally, mercurian tetrahedrite was observed at the Buca dell'Angina Cu deposit.

   According to Dini *et al*. (2001), the hydrothermal remobilization and deposition of mercury in the Apuan Alps is directly related to the low-temperature conditions of the Apenninic tectono-metamorphic event, as indicated by fluid-inclusion studies (homogenization temperatures between 226° and 288°C).

From modular analysis to solid-state chemistry

   Modular crystal chemistry seems to be a powerful approach with which to compare complex structures that present great similarities, but are neither isotypes nor homologues. If one considers the unit-cell structure motif of a compound as its "crystal genetic code", from

a topological point of view (*i.e.*, considering relative cation-to-anion positions, but excluding chemical differences, as well as split positions), rouxelite and kobellite present about 90% of the same crystal genetic code (*i.e.*, 90% of their structure motifs are homeotypic). A similar situation was pointed out between scainiite and pellouxite (Moëlo *et al*. 2000, Palvadeau *et al*. 2004), which also have 90% of their genetic code in common. This high degree of configurational similarity within each pair of sulfosalts provides direct evidence of plesiotypy, as defined by Makovicky (1997) and described by Ferraris *et al*. (2004).

FIG. 9.   Paving with the same type of tiles of the projections of the crystal structures of rouxelite (a) and kobellite (b). To enhance the contrast, some tiles have been colored (green or pink), as well as some residual interstices (yellow). There is a symmetrical mode of paving in kobellite.
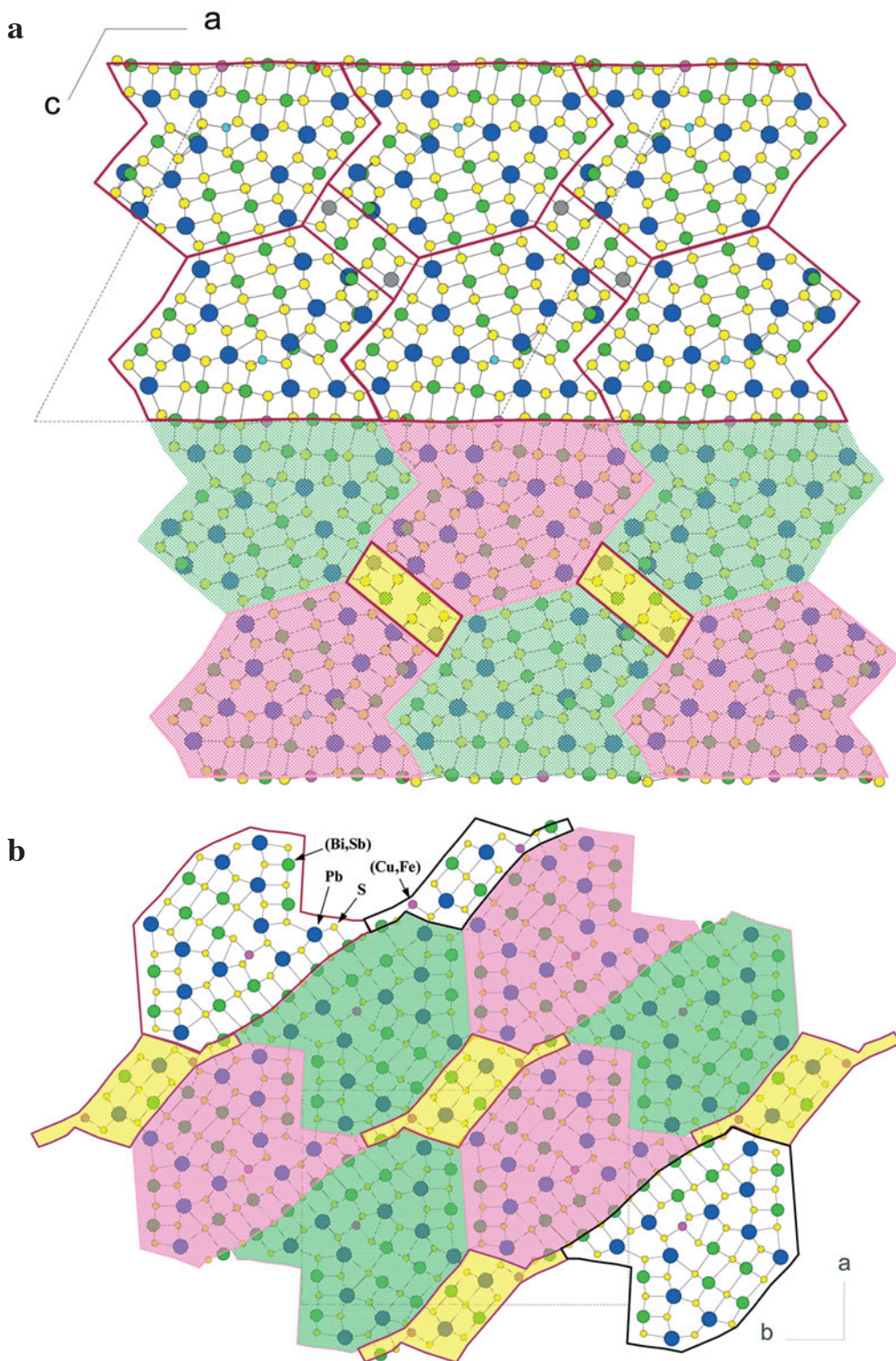
The high degree of modular complexity of a crystal structure enhances the number of plesiotypic relationships. Rouxelite is plesiotypic not only with kobellite, but also with neyite, as well as with $K_{1.25}Pb_{3.50}Bi_{7.25}Se_{15}$ and isostructural synthetic seleniosalts (Choi *et al*. 2001). These seleniosalts belong to the vast plesiotypic series $A_m[M'_{1+l}Se_{2+l}]_{2m}[M''_{2l+n}Se_{2+3l+n}]$ (A = K, Rb, Cs, Sr, Ba; M' = Pb, Sn; M'' = Sb, Bi; Mrotzek & Kanatzidis 2003), which presents very interesting thermoelectric properties (Choi *et al*. 2001). The structure of rouxelite thus appears as a new crystal-chemical model, controlled by specific minor chemical elements, of special interest in the search of new compounds for applications in solid-state chemistry. From this viewpoint, a first step would be the synthesis of rouxelite and possible Bi- or Se-dominant isotypes.

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